# Time evolution of $In_2O_3$ rod-like structures in metalorganic chemical vapor deposition process

HYOUN WOO KIM*, NAM HO KIM, SEUNG HYUN SHIM, JU HYUN MYUNG
*School of Material Science and Engineering, Inha University, Yong Hyun Dong, Nam Gu, Incheon 402–751, Republic of Korea*
*E-mail: hwkim@inha.ac.kr*

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Transparent conduction oxide (TCO) materials exhibit high electrical conductivity, high optical transparency, and high infrared reflectivity. Among TCO materials, indium oxide ($In_2O_3$), which is an *n*-type semiconductor with a wide bandgap, has become the choice for many device applications [1–6]. Since low-dimensional materials have been actively investigated, stimulated by the need for understanding their novel physical and chemical properties different from those in bulk state and for their potential applications to new types of electronic, magnetic, optic, photocatalytic, and energy storage devices [7, 8], the main streams of the present studies have been focused on preparing low-dimensional crystals with special morphologies, such as nanorods, nanowires, dendrite crystals, etc. Accordingly, many means have been developed for the synthesis of the $In_2O_3$ one-dimensional (1D) structures [9–19]. In this work, in order to synthesize the $In_2O_3$ rod-like structures on silicon (Si) substrates, we have employed the metalorganic chemical vapor deposition (MOCVD) method. We have investigated the variation of the structural properties by conducting the same experiment with different growth time.

The products were grown on (001)-oriented Si by MOCVD. A schematic illustration of the MOCVD system was previously reported [20, 21]. The triethylindium (TEI) with Ar carrier gas was supplied into the reactor as indium source and oxygen ($O_2$) was used as oxidizer. The Ar carrier gas flowed through the TEI bubbler maintained at 35 °C. The flow rates of $O_2$ and Ar carrier gases, respectively, were 5 standard cubic centimeters per minute (sccm) and 20 sccm, with the growth time ranging from 5 to 60 min. The substrate temperature was set to 350 °C. The structural properties were investigated by X-ray powder diffraction (XRD), operating on a Philips X'pert MPD X-ray diffractometer with CuK$\alpha$ radiation. The morphologies of the product were examined by scanning electron microscopy (SEM) (JEOL, JSM-6700F).

Fig. 1 shows the cross-sectional SEM images of the products, indicating that the thicknesses of the film-like structures deposited with the growth time of 5, 10, 20, and 60 min, respectively, are approximately 1.0, 2.9, 3.8, and 12.5 $\mu$m. SEM images indicate that the products grown for 10, 20, and 60 min consist of the rod-like structures, while the product grown for 5 min do not. Figs. 2a–d show the plan-view SEM images of the products, respectively, with a growth time of 5, 10, 20, and 60 min. From the top view, we reveal that the side length of the triangular cross section of the rod-like structures increases with increasing the growth time in the range of 10–60 min. It is noteworthy that the rod-like structures grown for 60 min are more sparsely distributed, compared to those grown for 10–20 min. By ultrasonically dispersing the products in the sample preparation for transmission electron microscopy, we found that the rod-like structures were isolated from each other (not shown here).

Fig. 3 shows the XRD spectra of the products with the growth time in the range of 5–60 min. Apart from the Si(004) diffraction peak (not shown here), the $\theta$–$2\theta$ scan data from the products exhibit a main peak at 30.6°, corresponding to (2 2 2) diffraction peak of cubic bixbyite $In_2O_3$ phase (JCPDS 44-1087). The (2 2 2) diffraction peak is relatively strong compared to the neighbouring diffraction peaks, revealing a high degree of texturing in the [111] direction.

Since close examination of Fig. 1b–d implies that there exist the predeposited films between the Si substrates and the rod-like structures, we surmise that the layer has been formed before the formation of the rods. The products grown for 5 min (Fig. 1a) is found to be a film without the rod-like structures, confirming the above suggestion. During the process, the rod-like structure grows toward the preferred [1 1 1] direction with the structure being the crystallographically preferred geometry. Since Fig. 2 reveals that the cross-sectional area of the rod increases with increasing the growth time, we surmise that the rod surviving the elimination becomes thicker, with some weakly developing rods eliminated. Preliminary experiments with a substrate temperature ranging from 200 to 300 °C resulted in a flat $In_2O_3$ film. The anisotropic growth behavior, producing an $In_2O_3$ rod of a high aspect ratio, may be

* Author to whom all correspondence should be addressed.

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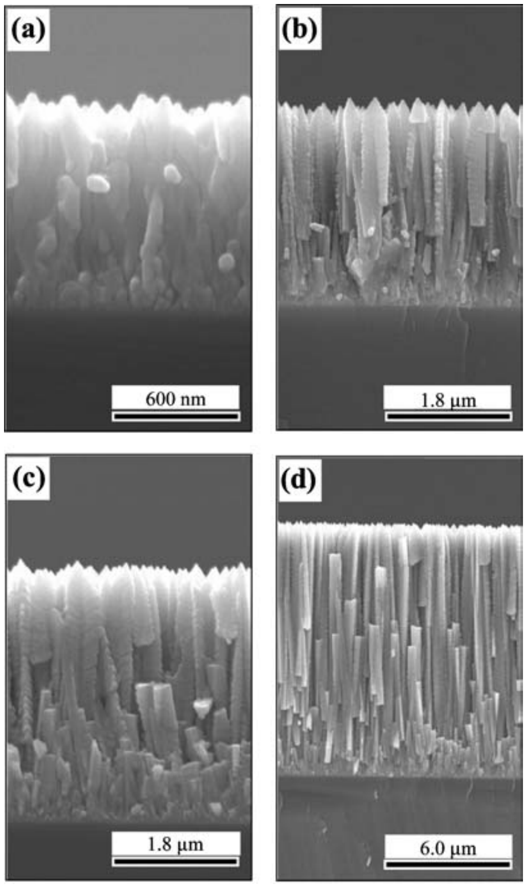


*Figure 1* Cross-sectional SEM images of the products with a growth time of (a) 5, (b) 10, (c) 20, and (d) 60 min.

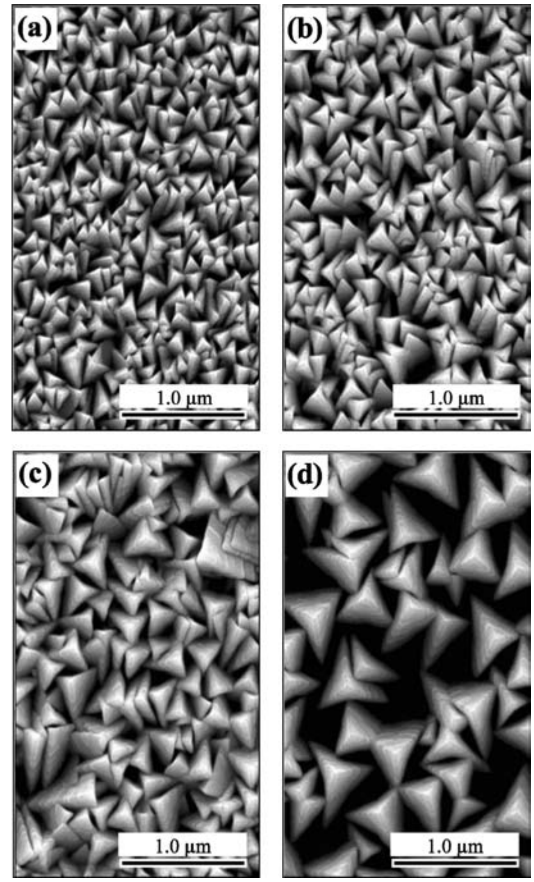


*Figure 2* Plan-view SEM images of the products with a growth time of (a) 5, (b) 10, (c) 20, and (d) 60 min.

enhanced at higher substrate temperature (350 °C), possibly due to the faster diffusion of In and O species. Since the formation process of the as-obtained structures is not clear enough, more work is still required.

In summary, in the growth process of $In_2O_3$ structures using the TEI as a precursor in the presence of oxygen, we have varied the growth time while keeping other conditions unchanged. SEM images indicate that

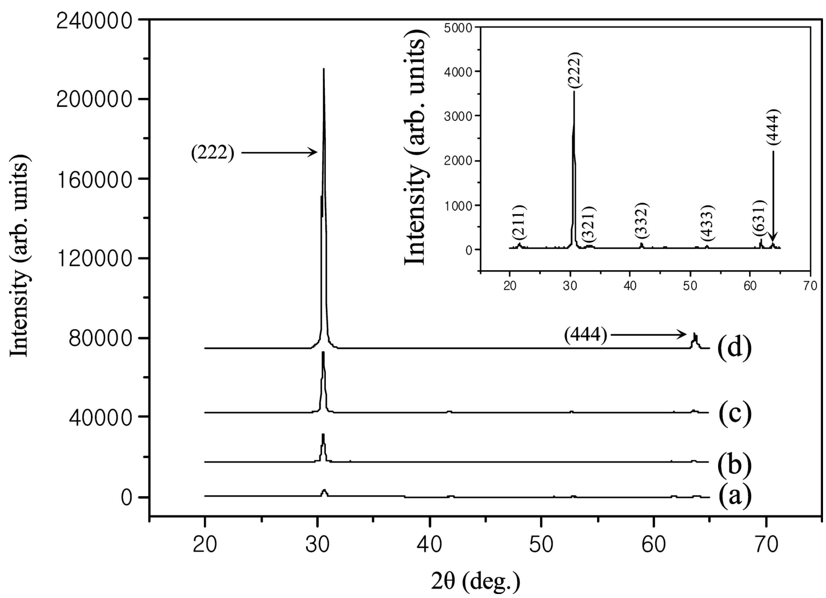


*Figure 3* XRD patterns of as-synthesized products with a growth time of (a) 5, (b) 10, (c) 20, and (d) 60 min. (Inset: Enlarged view of the XRD pattern corresponding to the products grown for 5 min.)

while the obtained product is a film with a growth time of 5 min, the products grown for 10–60 min consist of the rod-like structures. XRD analysis reveals that the $In_2O_3$ structures are cubic structures with the predominant [111] orientation.


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